SAMSO-TR-70-101

ELECTRON DETACHMENT FROM F^- ION IN A SHOCK-HEATED CESIUM FLUORIDE-ARGON MIXTURE

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AVCO EVERETT RESEARCH LABORATORY

AMP 301

December 1970

jointly sponsored by

ADVANCED RESEARCH PROJECTS AGENCY
DEPARTMENT OF DEFENSE
ARPA Order #1092

and

SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
DEPUTY FOR RE-ENTRY SYSTEMS (SMY)
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ELECTRON DETACHMENT FROM F^- ION IN A SHOCK-HEATED CESIUM FLUORIDE-ARGON MIXTURE*†

by

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a division of
AVCO CORPORATION
Everett, Massachusetts

* This research was supported by the Advanced Research Projects Agency of the Department of Defense and Space and Missile Systems Organization, Air Force Systems Command and was monitored by Space and Missile Systems Organization, Air Force Systems Command under Contract F04701-70-C-0128.

† Submitted to Chemical Physical Letters

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FOREWORD

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"This research was supported by the Advanced Research Projects Agency of the Department of Defense and Space and Missile Systems Organization, Air Force Systems Command and was monitored by Space and Missile Systems Organization, Air Force Systems Command under Contract F04701-70-C-0128." The secondary report number as assigned by AERL is Avco Everett Research Laboratory AMP 301. The Air Force program monitor for this contract is Capt. R. W. Padfield, USAF, Project Officer, Environmental Technology Branch, RNSE.

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Capt. R. W. Padfield, USAF,
Project Officer
Environmental Technology Branch,
RNSE

ABSTRACT

An experimental determination has been made of the rate of electron detachment from F^- in shock-heated mixtures of cesium fluoride and argon. The detachment rate is found to increase exponentially with temperature, indicating an activation energy comparable to the electron affinity of F^-. The rate constants for the reactions $F^- + Ar \xrightarrow{k(Ar)} F + Ar + e$ and $F^- + Cs^+ \xrightarrow{k(Cs^+)} F + Cs^+ + e$ have been found to be $1.2 \times 10^{-11} e^{-40,000/T}$ cm^3/sec and $5.6 \times 10^{-9} e^{-40,000/T}$ cm^3/sec respectively, where T is in degrees Kelvin.

We have studied the collisional detachment rate of electrons from F^- in a shock tube environment following the nonequilibrium overshoot of ions in the dissociation of CsF in argon. F^- collisional detachment cross sections have been measured at energies above ~ 100 eV.[1] The cross sections measured were found to remain very high down to less than 100 eV in violation of the adiabatic criterion.[2] We have now extended the range of these cross-section measurements to much lower energies.

The extensive work of Berry, et al.,[3,4] has shown that the small difference between ionization potential of the alkali atom and the electron affinity of the halide atom results in the crossing of the potential energy curve for the neutral atoms and the coulomb curve for the ions at large internuclear separation causing a violation in the non-crossing rule. The thermal dissociation of an alkali halide molecule leads to a nonequilibrium population of the primary dissociation products (Cs^+ and F^- in our case).

Thus, under the conditions of our experiment, the CsF dissociates in the shock tube almost entirely into Cs^+ and F^- by the following reaction

$$CsF + Ar \rightarrow Cs^+ + F^- + Ar. \qquad (1)$$

After the CsF dissociates, we follow the decay of the F^-. We also monitor the Cs^+ density and since we know the argon density from the initial gas pressure and the shock speed, we are

able to solve the equation for the logarithmic time derivative of the F^- density

$$\frac{1}{[F^-]} \frac{d[F^-]}{dt} = -k(Ar)[Ar] - k(Cs^+)[Cs^+] \qquad (2)$$

for both rate constants k(Ar) and $k(Cs^+)$, where we assume that the major processes leading to the collisional detachment of F^- are[5]

$$F^- + Ar \rightarrow F + Ar + e \qquad (3a)$$

and

$$F^- + Cs^+ \rightarrow F + Cs^+ + e \; . \qquad (3b)$$

CsF is introduced, with the argon, into our shock tube as a dust of very small granules. The CsF densities are typically 1% or less of the argon density. The mixture is heated by the shock wave causing the dust to evaporate and subsequently dissociate. The time duration of both evaporation and dissociation of the CsF has been seen to be short when compared with that of the F^- collisional detachment under our experimental conditions.

Observations of the F^-, Cs^+ and electrons have been made in both absorption and emission experiments. The various diagnostics used are summarized in Table I. It should be noted that several diagnostics have been used simultaneously in taking these measurements. In our most recent measurements, we have measured the F^- absorption signal at wavelengths between 3100 Å and 2100 Å since in this region the photoabsorption cross section for F^- is

TABLE I

SUMMARY OF VARIOUS MEASUREMENTS*

Measurement	Quantity Derived	Quantity Measured ‡	Relevant Equation	Wavelength of Measurement	Detection System
F^- absorption	$[F^-]$	$I=I_o e^{-[F^-]\sigma\ell}$	$[F^-]=[F^-]_o e^{-k(T)[Ar]t}$	(a) 3440 Å (b) 3100 Å to 2100 Å	(a) 3 pass - 3440 Å filter - S11 photo-tube (b) 1 pass - double monochromator - solar blind photo-tube. Incident and reflected shock
Cs^+ emission free-bound	$[Cs^+][e]$	$I \propto [e][Cs^+]$	$Cs^+ = \text{const}$ $[e]=[F^-]_o(1-e^{-k(T)[Ar]t})$	4000 Å	4000 Å filter with S11 photo-tube
Bremsstrahlung emission †	$[e]$	$I \propto [e]$	$[e]=[F^-]_o(1-e^{-k(T)[Ar]t})$	2.5 μ	Liquid N_2 cooled InSb photovoltaic element

*[ ] = density

$[\cdot]_o$ = initial density

† The relation for I holds if ion density is less than a few by 10^{-3} of neutral gas density.

‡ $\sigma\ell$ = absorption cross section per F^- ion multiplied by the length of the absorption path.

several times larger than at 3445 Å.[6,7] The light source is a xenon flash lamp which is pulsed so that its maximum intensity is reached as the shock front passes the detector. The detector used is a double monochrometer with a solar blind phototube. Measurements were simultaneously made of the free-bound $Cs^+ + e$ emission in order to give us a measure of the Cs^+ concentration.

The results of these measurements are plotted in Fig. 1. We have rewritten Eq. (2) in terms of a total measured rate constant as

$$\frac{1}{[F^-]} \frac{d[F^-]}{dt} = k(T)\,[Ar] \tag{4}$$

where

$$k(T) = k(Ar) + k(Cs^+) \frac{[Cs^+]}{[Ar]} \tag{5}$$

and assuming the same T dependence for both reactions

$$= \left\{ \alpha + \beta \frac{[Cs^+]}{[Ar]} \right\} e^{-40,000/T} \tag{6}$$

$$k(Ar) = \alpha\, e^{-40,000/T} \tag{7a}$$

$$k(Cs^+) = \beta\, e^{-40,000/T} . \tag{7b}$$

Thus, the intercept of Fig. 2 gives α and the slope β. If we substitute these values into Eqs. (7a) and (7b), we find

$$k(Ar) = 1.2 \times 10^{-11}\, e^{-40,000/T}\ cm^3/sec \tag{8a}$$

and

$$k(Cs^+) = 5.6 \times 10^{-9}\, e^{-40,000/T}\ cm^3/sec . \tag{8b}$$

We have plotted our measured rate constant k(Ar) as a function of 1/T in Fig. 2. It is seen that the best fit

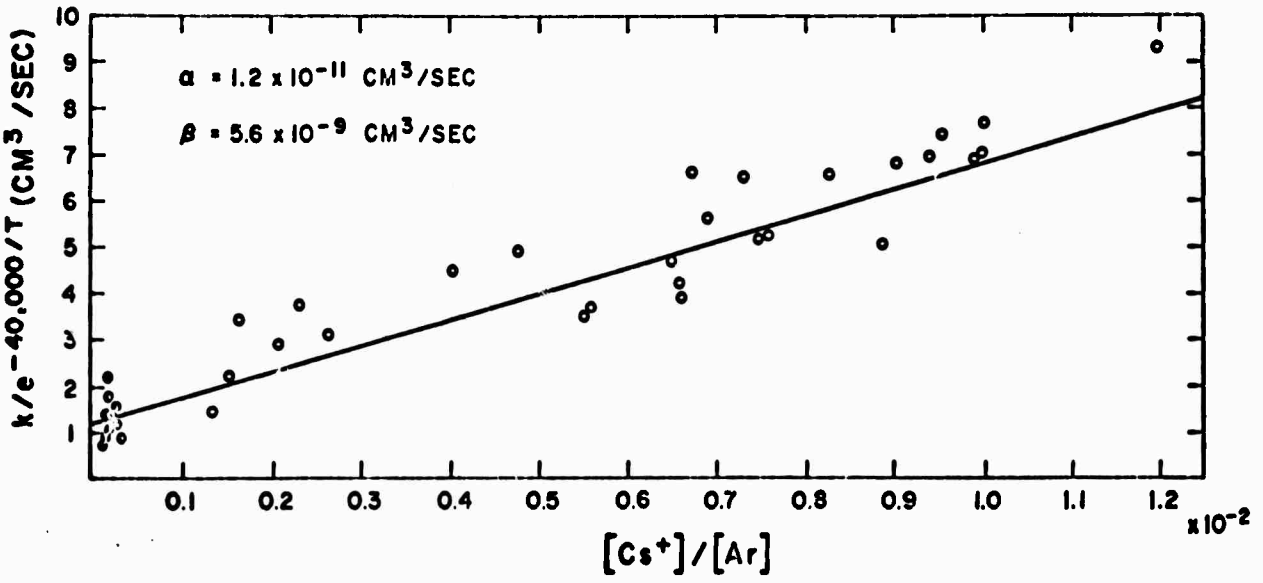

Fig. 1 This is a plot of our measured rate constant [k(T) of Eq. 6], with the temperature dependence divided out as a function of the fractional concentration of Cs^+ to Ar. The y intercept gives the value of $k(T)/e^{-40,000/T}$ at zero [Cs^+] [i. e., α of Eq. (7a)] whereas the slope determines β of Eq. (7b). The open circles are incident shock measurements and the closed circles are reflected shock measurements.

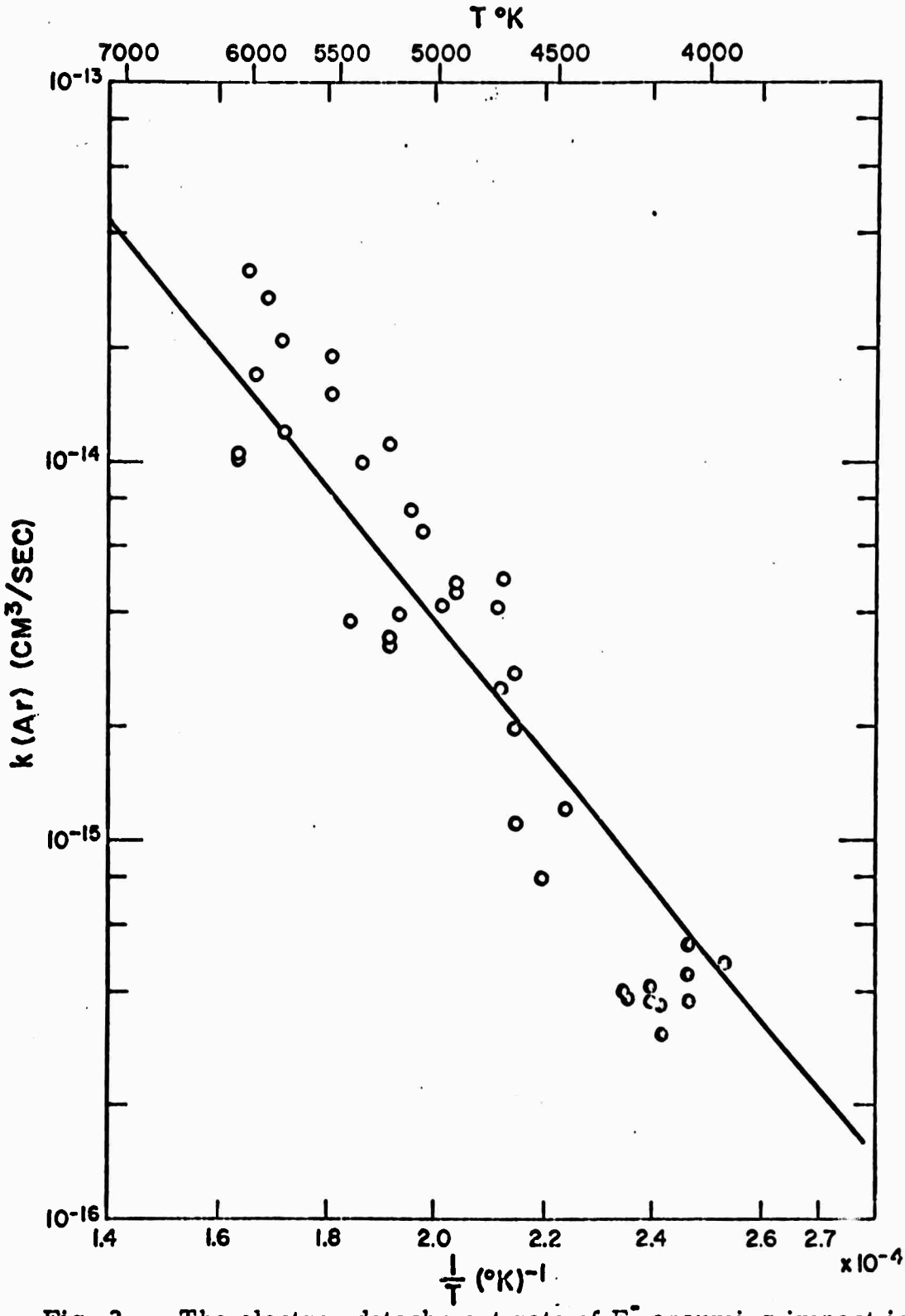

Fig. 2 The electron detachment rate of F^- assuming impact ionization by the atomic argon [K(Ar) cm^{-3}/sec] as a function of $10^4{}^oK/T$. The effect of the Cs^+ (as determined from Fig. 1) has been subtracted. The solid line shows the dependence of a detachment rate having an activation energy equal to the electron affinity of F^-. The open circles are incident shock measurements and the closed circles are reflected shock measurements.

to these points gives a slope which is consistent with an activation energy equal to the electron affinity of fluorine.

We thus find ourselves in agreement with some of the results of the higher energy measurements, i.e., that the collisional detachment cross sections remain larger than would be theoretically expected down to very low velocities.[2] We can also compare our results to those of Berry, et al.,[3] who find for the reaction

$$Br^- + Ar \xrightarrow{k'(Ar)} Br + Ar + e \qquad (9)$$

that (in our notation)

$$k'(Ar) = 5.8 \times 10^{-11}\, e^{-39,000/T}\ cm^3/sec, \qquad (10)$$

in good agreement with our Eq. (8a).

ACKNOWLEDGMENTS

The authors are indebted to Dr. E. Sutton who proposed this experiment and guided the initial phases of the program and to R. Jonkman for much work performed in the initial phase. Significant technical help and guidance was received from K. Wray, Chairman of the Avco Everett Research Laboratory Atomic Physics Committee. We also acknowledge assistance from J. Keck, M. Camac and J. D. Teare. Numerical nonequilibrium calculations of shock front conditions were provided by G. E. Caledonia. The technical assistance received from J. W. Martz, Jr., in operation of the shock tube and other experimental apparatus was a most important contribution to this program.

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2. Branscomb, L. M., Adv. in Electronics & Electron Phys., Vol. IX, Academic Press (1957).

3. Berry, R. S., et al., J. Chem. Phys. 49, 127 (1968).

4. Ewing, J. J., Milstein, R. and Berry, R. S., 7th Shock Tube Symp., Toronto, Canada (1969).

5. Processes of the type $F^- + e \rightarrow F + 2e$, $F + F^- \rightarrow F_2 + e$ and $F + F^- \rightarrow F + F + e$ are not considered since if these processes were large, our resultant F^- decay curve would show an incubation time corresponding to the initially low electron density and fluorine density. This shape is not observed. The reaction $F^- + F^- \rightarrow F + F^- + e$ is assumed to be negligible when compared with (3b).

6. The results of the measurements are to be published elsewhere.

7. E. W. Evans and B. Kivel, Avco Everett Research Laboratory Research Note 827 (Avco Everett Research Laboratory, Everett, Mass., 1969).

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DOCUMENT CONTROL DATA - R&D

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1. ORIGINATING ACTIVITY (Corporate author) Avco Everett Research Laboratory 2385 Revere Beach Parkway Everett, Massachusetts	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3. REPORT TITLE

Electron Detachment From F^- Ion in a Shock-Heated Cesium Fluoride-Argon Mixture

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

AMP 301

5. AUTHOR(S) (Last name, first name, initial)

A. Mandl, E. W. Evans and B. Kivel

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
December 1970	9	7

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
F04701-70-C-0128 b. PROJECT NO.	AMP 301
c. d.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SAMSO-TR-70-101

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DD FORM 1 JAN 64 1473

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14. KEY WORDS	LINK A		LINK B		LINK C	
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